Appendix 3

Closure by Stability Monitoring and Petroleum Closure by Attenuation Modeling

A3.0 Introduction

When attempting to demonstrate plume stability for closure, stability monitoring must be conducted to ensure that constituents will not leave the area of property control at concentrations that exceed residential closure levels. Plume stability may be demonstrated by a default or a nondefault method. This appendix presents the default stability monitoring method to demonstrate plume stability.

All stability monitoring methods require that properly designed and installed ground water monitoring wells be placed at appropriate locations to correctly evaluate the plume. In the default method, a minimum of two types of monitoring wells are required: messenger wells and perimeter of compliance (POC) wells. Background wells and sentinel wells may also be required if upgradient and downgradient COC concentrations need to be evaluated. Figure A3-1 shows possible locations for the four types of monitoring wells. Requirements for each type of well are discussed below.

- **Messenger wells** are located in the internal area of the plume, downgradient from the source, within the 2-year ground water time-of-travel distance. At a minimum, one messenger well must be located adjacent to the source, and a second well must be located between the first messenger well and the 2-year time-of-travel distance of the plume. When petroleum closure by attenuation is being used (see Section A3.2), one messenger well must be located within 1-year travel time from the source. To demonstrate ground water closure, an area of concern will normally require two to four messenger wells. Some large, or multilobed contaminant plumes may require more than four messenger wells. All messenger wells must be located (1) as near to the center flow line or flow path as possible and (2) in an area where the COC concentrations are suspected to be highest and to significantly exceed closure levels.

- At least three **POC wells** should be located hydraulically downgradient from the messenger wells and from the principal closure areas. POC wells must be located as follows:

  - In an area of the plume where dissolved COC concentrations are expected to exceed estimated quantification limits (EQL) for at least 75 percent of the monitoring episodes

- – In an area where COC concentrations approximate the closure level

- – In an area where it is possible to monitor the contaminant plume after it has passed through the source and messenger well areas

- **Sentinel wells** should be installed if the potential exists for increased risks to any receptors. Sentinel wells are located hydraulically downgradient from the POC wells and along a line between the source and any potential receptors. Sentinel wells may not be required if no downgradient receptor exists; however, sentinel wells are highly recommended because they can clearly indicate an expanding plume.

- **Background wells** are placed upgradient of the area of concern and out of the zone of influence of the source. Background wells are essential to understanding the upgradient influence of COCs. If both upgradient and downgradient concerns exist at a site, a minimum of one background well is required. However, additional background wells may be recommended based on the discussions below.

Additional wells and piezometers may also be needed to characterize hydrogeologic conditions. If the wells do not meet appropriate criteria, or if site conditions change, previously installed wells may no longer produce samples that adequately represent the plume being monitored. In such cases, new wells may be required, or existing wells may be redesignated to serve a different monitoring function than originally intended.

Some wells must be located within specific ground water time-of-travel distances from the source. Before wells are installed, the advective flow velocity of ground water at the site must be estimated to ensure that the new wells will meet the ground water time-of-travel requirements. This approach will allow sufficient time during monitoring to ensure that ground water from the closure area reaches key monitoring wells.

In the default approach, the Mann-Kendall trend test must be used to define the COC concentration trend in individual monitoring wells (EPA 1996, EPA/600/R-96/084)

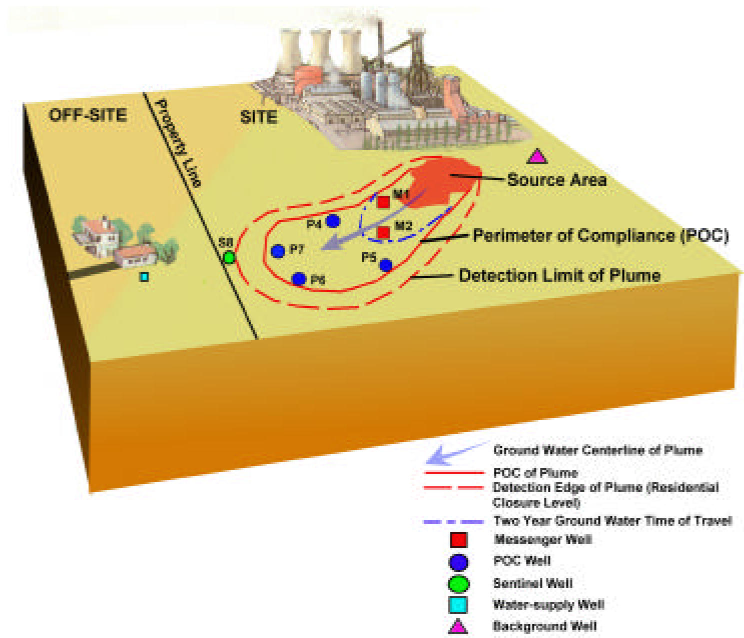

Figure A3-1. Monitoring Well Location

A graph of time versus concentration (time series plot) must be constructed and maintained for each COC at each well throughout the monitoring period. This will facilitate determining any potential trends in the data.

A3.1 Closure by Stability Monitoring

Stability monitoring evaluates screening data to determine the concentration trend for each COC at individual monitoring wells. The primary concern in a stability demonstration is whether COC concentrations are increasing or decreasing at individual monitoring wells. Numerical changes in COC concentration levels can often appear insignificant from one quarterly monitoring event to another. To determine if the contaminant plume is stable or migrating, ground water monitoring data must be analyzed statistically. The Mann-Kendall trend test is used to determine the concentration trend at each well for each COC. The plume is considered to be expanding if the trend test results indicate that any COC concentration is increasing as follows:

- Two or more messenger wells
- Any POC well
- Any sentinel well.

If the plume is expanding, a POC remedial plan must be developed and implemented. If the plume is stable (that is, no trend is indicated by the Mann-Kendall trend test) or decreasing (a negative trend in the Mann-Kendall trend test), then the plume is considered stable. In such cases, monitoring should continue and quarterly data should be evaluated for closure eligibility (see Section A3.1.5).

Closure by stability monitoring does not rely on any specific plume age considerations. Professional judgement should be applied to make the initial decision of whether a plume may be stable. The trend tests used to verify stability will not show a stable or decreasing trend if the plume has not had sufficient time to stabilize. Free product must be removed to the extent practicable, and any remaining COCs must not create an expanding plume.

Figure A3-2 shows a flowchart for stability monitoring. In general, the first step involves assessing the potential for plume stability. A minimum of 8 quarters of monitoring data must be evaluated at the messenger and POC wells. The Mann-Kendall trend test is used to assess the trend in the plume for each COC at each individual well. If this evaluation indicates that the plume is stable in COC concentrations, then the stability monitoring period can begin. The wells must then be monitored for the next 5 years and tested annually using the Mann-Kendall trend test to verify that the plume continues to remain stable or decrease in COC concentrations. If the above conditions are met at the end of the 5-year stability monitoring period (7 years total), the area of concern may be eligible for closure.

Stability monitoring closure for ground water contaminant plumes involves the following steps: (1) starting the stability clock, (2) stability monitoring, (3) the Mann-Kendall trend test, (4) additional data collection, and (5) closure eligibility.

A3.1.1 Starting the Stability Clock

The stability clock “starts” with the first quarterly sampling in the stability monitoring period. However, before stability monitoring can begin, the following activities must be performed:

1. A complete and adequate investigation of the nature and extent of contamination

2. Establishment of the POC

3. Placement and initial sampling of messenger and POC wells

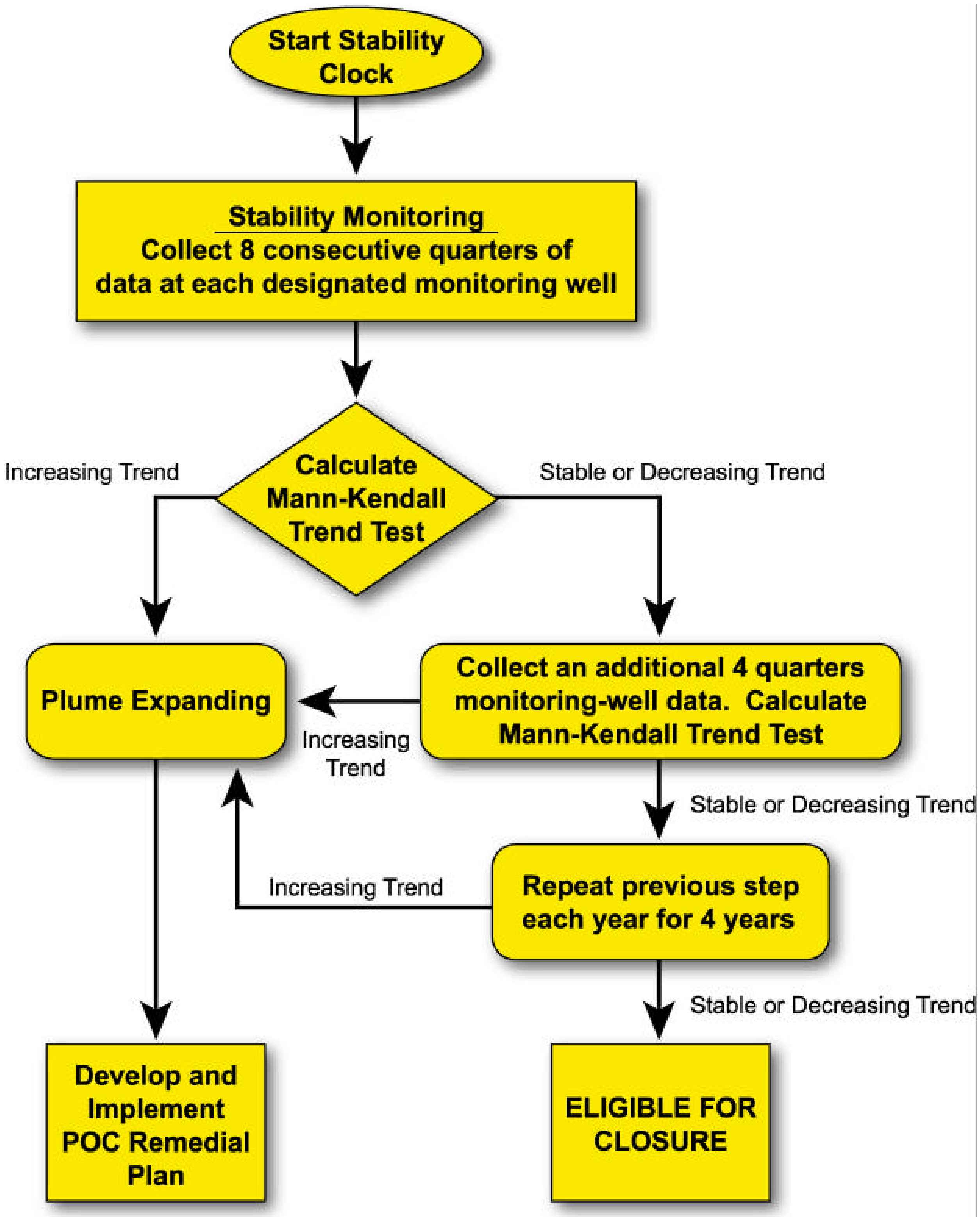

Figure A.3-2. Stability Monitoring Closure for Ground Water Contaminant Plumes

When evaluating an existing plume using historical monitoring data, the start date for the stability clock will be the first quarter of a consecutive and continuing trend of quarterly data showing stability (using the Mann-Kendall trend test). It may be more practical to begin with the most recent year's data and work back in time until the beginning of the stable trend is identified. Historical data should be treated in the same way that new data would be treated (see Section A3.1.2). In addition, existing site information must be evaluated to ensure that all of the required activities have been completed.

A3.1.2 Stability Monitoring

Stability monitoring requires 8 consecutive quarters of ground water monitoring data from wells designated for stability closure (messenger and POC wells). Eight quarters of data are required to provide sufficient data for trend tests. To minimize the possibility of an expanding plume during stability monitoring, a remedial plan must be developed and implemented if monitoring data indicate four consecutive increases at any POC well. If data from POC wells do not show four consecutive increases, the Mann-Kendall trend test may be conducted to further evaluate plume stability.

A3.1.3 Mann-Kendall Trend Test

This section gives a general procedure and examples for determining if COC concentrations are increasing at an individual ground water monitoring well. This determination is reached using the Mann-Kendall trend test. The general procedure for the test is provided in the box below.

Mann-Kendall Trend Test General Procedure

1. Collect ground water samples from each well for at least eight consecutive quarters.
2. List the data in the order collected over time: x_1, x_2, ... x_n, where x_i is the measured concentration at time t_i . For values below the EQL, use EQL/2. Construct a data matrix as shown in the Table A3-1 and examples.
3. Compute the signs of all the ordered differences, as shown in Table A3-1 and examples.
4. Compute the Mann-Kendall statistic, *S*, which is the number of positive changes minus the number of negative changes in the data sequence. Zeros that result from two consecutive values being identical do not enter into the calculation.
5. If there are between 8 and 10 measurements in the sequence, use Table A3-2 to find the trend probability *P* corresponding to sample size *n* and the absolute value of the Mann-Kendall *S*.

   If there are 11 or more measurements in the sequence, use the normal approximation in the Large Sample example to determine a *z (P)* value.
6. The " value for this test is 0.10 for the first two trend tests and 0.05 afterward. If $S > 0$ and $P <$ ", the null hypothesis of no increasing trend is rejected, and concentrations are considered to be increasing at this well. Otherwise, the well concentrations are considered stable.

Table A3-1. Data Matrix for Calculating the Mann-Kendall Statistic, *S*

Time	t_1	t_2	t_3	t_4	t_5	No. of + signs	No. of - signs
Conc.	x_1	x_2	x_3	x_4	x_5		
x_1		$x_2 - x_1$	$x_3 - x_1$	$x_4 - x_1$	$x_5 - x_1$		
x_2			$x_3 - x_2$	$x_4 - x_2$	$x_5 - x_2$		
x_3				$x_4 - x_3$	$x_5 - x_3$		
x_4					$x_5 - x_4$		
					Totals:	Total +'s	Total -'s

NOTE: For compactness, this table shows a sequence of five measurements; however, at least eight are required to demonstrate stability. When there are *n* measurements, there are *n* entries in the table. When two successive concentrations are identical, the resulting zero difference is neither positive nor negative, and it is ignored.

Two examples of using the Mann-Kendall trend test to calculate plume stability are provided below. The first example illustrates using the test for a small sample size (n = 10). The second example is for a larger sample size and is considered the normal approximation.

Small Sample Example

The following example has a sample size of 10 measurements (n = 10) in the data sequence:

Time	1	2	3	4	5	6	7	8	9	10	No. of +	No. of -
Conc.	9	9	11	5	12	20	18	18	17	22		
9		0	+	-	+	+	+	+	+	+	7	1
9			+	-	+	+	+	+	+	+	7	1
11				-	+	+	+	+	+	+	6	1
5					+	+	+	+	+	+	6	0
12						+	+	+	+	+	5	0
20							-	-	-	+	1	3
18								0	-	+	1	1
18									-	+	1	1
17										+	1	0
									Totals:		35	8

For this example, S = 35 - 8 = 27. With n = 10 and S = 27, Table A3-2 yields a probability value (P) = 0.0083.

Because P = 0.0083 is less than " = 0.10, concentrations are considered to be increasing for this well. Because the plume may be expanding, and a remedial plan may be required. See *Practical Methods for Data Analysis-EPA QA/G-9* (EPA 1984).

In cases yielding a P value greater than " = 0.10, no trend in concentrations would be demonstrated for this well.

Table A3-2: Probabilities for Small-Sample Mann-Kendall Trend Test

S	n = 4	n = 5	n = 8	n = 9	S =	n = 6	n = 7	n = 10
0	0.625	0.592	0.548	0.54	1	0.5	0.5	0.5
2	0.375	0.408	0.452	0.46	3	0.36	0.386	0.431
4	0.167	0.242	0.360	0.381	5	0.235	0.281	0.364
6	0.042	0.117	0.274	0.306	7	0.136	0.191	0.3
8		0.042	0.199	0.238	9	0.068	0.119	0.242
10		0.0083	0.138	0.179	11	0.028	0.068	0.19
12			0.089	0.130	13	0.0083	0.035	0.146
14			0.054	0.090	15	0.0014	0.015	0.108
16			0.031	0.060	17		0.0054	0.078
18			0.016	0.038	19		0.0014	0.054
20			0.0071	0.022	21		0.0002	0.036
22			0.0028	0.012	23			0.023
24			0.00087	0.0063	25			0.014
26			0.00019	0.0029	27			0.0083
28			0.000025	0.0012	29			0.0046
30				0.00043	31			0.0023
32				0.00012	33			0.0011
34				0.000025	35			0.00047
36				0.0000028	37			0.00018
					39			0.000045

Large Sample Example (Normal Approximation)

The example below is similar to the Small Sample test, but it applies to cases with 11 or more measurements in the sequence. The procedures are as follows:

Step 1:Calculate the Mann-Kendall *S* statistic.

Time	1	2	3	4	5	6	7	8	9	10	11	12	No. of +	No. of -
Conc.	9	9	11	5	7	11	12	20	18	18	18	22		
9		0	+	-	-	+	+	+	+	+	+	+	8	2
9			+	-	-	+	+	+	+	+	+	+	8	2
11				-	-	0	+	+	+	+	+	+	6	2
5					+	+	+	+	+	+	+	+	8	0
7						+	+	+	+	+	+	+	7	0
11							+	+	+	+	+	+	6	0
12								+	+	+	+	+	5	0
20									-	-	-	+	1	3
18										0	0	+	1	0
18											0	+	1	0
18												+	1	0
											Totals:		52	9

Hence, $S = 52 - 9 = 43$.

Here, The Mann-Kendall *S* statistic is calculated just as before, but a calculated normal approximation *z* value is substituted for the *P* value. To evaluate trends, the measured ***z*** value is then compared to the critical *z* value (from " = 0.10 or 0.05) to evaluate trends.

Step 2: Calculate SE_S

Calculate the standard error of *S* (SE_S) using one of the following formulas. If there are no repeated values (ties) use Equation A3-1 below.

Equation A3-1

$$SE_s = \left[\frac{n(n-1)(2n+5)}{18}\right]^{0.5}$$

If there are repeated values, use Equation A3-2.

Equation A3-2.

$$SE_S = \left\{ \frac{1}{18} \left[n(n-1)(2n+5) - \sum_{p=1}^{g} k_p (k_p - 1)(2k_p + 5) \right] \right\}^{0.5}$$

Where

g is the number of tied groups
k_p is the number of times the value in the group (p) is repeated

In the example above, n = 12, and g = 3 (for concentrations of 9, 11, and 18). There are 2 nines, 2 elevens, and 3 eighteens, so $k_1 = 2$, $k_2 = 2$, and $k_3 = 3$. Thus,

$$SE_S = \left[\frac{12(11)(29) - 2(1)(9) - 2(1)(9) - 3(2)(11)}{18} \right]^{0.5} = \sqrt{\frac{3726}{18}} = 14.3875$$

Step 3: Calculate z.

Calculate a standard normal ***z*** statistic, using the following equations and S values:

Equation A3-3a, b, and c

If S > 0, $z = \dfrac{S-1}{SE_s}$

If S = 0, z=0

If S < 0, $z = \dfrac{S+1}{SE_s}$

In the example given, S is positive, so the z value is calculated as follows:

$$z = \frac{43-1}{14.3875} = 2.919$$

Step 4: Compare z values

The critical z value z_{crit} = 1.282, based on a normal distribution with " = 0.10).

Because the calculated z (2.9) is greater than this critical z value (1.282), an increasing concentration trend is demonstrated for this well. Consequently, the plume may be expanding, and a remedial plan may be necessary.

In cases where the calculated z is smaller than z_{crit} , concentrations are considered stable. Stable individual wells contribute to a stable plume designation, which would allow stability monitoring to continue.

A3.1.4 Additional Data Collection

If the full stability monitoring period (7 years) has not passed, collect an additional four quarters of data at each well for each COC. For each COC at each well, calculate the Mann-Kendall trend test for (1) the most recent eight quarters of data and (2) all the data. The plume is considered to be expanding if test results indicate that any COC concentration is increasing at (1) two or more messenger wells, (2) any POC well, or (3) any sentinel well.

If the plume is expanding, a POC remedial plan must be developed and implemented. If the plume is not expanding, Step A3.1.3 should be repeated for each additional year remaining in the stability monitoring period.

A3.1.5 Closure Eligibility

If the plume is shrinking or stable, and the stability clock has been running for 7 years, the site may be eligible for closure under RISC. If the plume remains stable or demonstrates a decreasing trend for the full stability monitoring period, the site may be eligible for closure.

A3.2 Petroleum Closure By Attenuation Modeling

Research on petroleum indicates that a dissolved petroleum plume expands during the first 4 years regardless of site or area conditions; however, after several years, the leading edge of the plume will stabilize if attenuating conditions are present. Attenuation is defined as a reduction in petroleum constituent concentration or mass in ground water due to naturally occurring chemical and physical processes, including dispersion, sorption, biodegradation.

Attenuation modeling can only be performed for COCs originating from an eligible petroleum source, as described below. The model is simple and reliable if adequately calibrated and applied. In addition, it may allow closure of a site in as few as 3 years if the plume is decreasing. However, plume stability will not occur if free product or excess contamination exists at the source; therefore, all free product must be recovered to the extent practicable. Excavation and disposal of source material is one of the most effective strategies for ensuring eventual plume stability.

Sites eligible for attenuation modeling include the following:

1. The COC source was virgin petroleum fuel or virgin lubricating oil.

2. The contaminant plume is at least 4 years old. Responsible parties also may use this procedure if the plume age is unknown and is likely to be at least 4 years old.

3. Property control has been secured for all of the property affected by the contaminant plume, and proof of property control if provided to IDEM.

Data from petroleum-related plumes are subjected to statistical trend testing and monitoring to demonstrate plume stability. Sometimes the attenuation model will not accurately predict COC attenuation, in which case additional monitoring and stability testing will be needed. It may be necessary to adjust modeled attenuation rates to reflect actual attenuation rates for a period equal to the stability monitoring period (total time 7 years). In such cases, the area of concern may be eligible for closure by the standard stability monitoring procedures.

Before proceeding with attenuation modeling, all data must be reviewed to determine if the selected model is appropriate for the site conditions. The Mann-Kendall trend test, based solely on data from messenger wells, is generally the basis for determining if the model is appropriate.

Petroleum closure by attenuation modeling requires eight quarters of stable data. Once initial stability has been demonstrated, two options exist for pursuing petroleum closure: the stability monitoring method (see Section A3.1) or attenuation modeling.

When using the attenuation modeling option, a first-order decay model is applied to the stability monitoring data. Model results are then used to predict COC concentrations at each well for the following four quarters. If the predicted concentrations pass a goodness-of-fit test, data is collected for four additional quarters, and predicted and actual concentrations are compared statistically. If there is good agreement between the data sets (using the Root Mean Square Deviation Test), the site is eligible for closure.

The general procedure for petroleum closure by attenuation modeling is presented below. Overall, the procedure is similar to closure by stability monitoring; however, trend monitoring and decision data are subjected to different statistical tests. Attenuation modeling follows the same initial steps as stability monitoring, including (1) starting the stability clock (see Section A3.1.1), (2) stability monitoring (see Section A3.1.2), and (3) the Mann-Kendall trend test.

The model is not recommended if one or more messenger wells show an increasing trend. IDEM recommends constructing a sample-concentration-versus-time plot of the messenger well monitoring data as a decision aid.

If it is determined that it is not appropriate to use a model after the first eight quarters of monitoring, it is possible to monitor for an additional four quarters and try again. This approach may be appropriate if previous data trends appeared to support modeling.

When four more quarters of data have been collected, the Mann-Kendall trend test is once again used. To distinguish between long- and short-term trends, the Mann-Kendall trend test is applied to two different sets of data: (1) the entire data set and (2) data from the most recent 8 quarters. If either test indicates an expanding trend, the remedial plan must be developed and implemented.

If a model is not used, this monitoring and testing cycle must be performed for a 7-year period during which the plume is stable (Option 1). Option 2 requires modeling the contamination trend . If the trend tests during this period indicate that the plume is stable, closure may be applied for as described in Section A3.1.5. The sections below discuss concentration trend modeling, the goodness-of-fit test and verification modeling by the root-mean-square deviation test.

A3.2.1 Concentration Trend Modeling

The method for calculating, testing, and verifying concentration trends may be predicted from the first-order decay model expressed in Equation A3-4.

Equation A3-4 $C = C_0 \exp^{(-kt)}$

Where

C	=	Concentration at time t
C_0	=	Concentration at time 0
k	=	Attenuation rate [day-1]
t	=	time [days]

Although this model is often calibrated by solving the equation in natural logs using linear regression on the logarithms, that procedure produces biased results that may not fit future values well (see Miller 1984). In addition, "transformation-bias correction" suggested by Miller and others does not work well, except with very large sample sizes (Parkhurst, ES&T 1998). Therefore, the model should be calibrated by nonlinear regression. This regression is accomplished by finding the values of C_0 and k that minimize the sum (S) of the squared deviations.

Equation A3-5. $S = \sum_{t=0}^{N} \left[C_i - C_0 \exp(-kt_i)\right]^2$

1. Combine with A3-4, add "S = sum of the squared deviations" to parameter list.
2. S is summed from i = 0 to N, not from N.

Note: C = Ci]

This calculation is included in the RISC software package.

The model is calibrated for "fit" using eight or more quarters of messenger well stability monitoring data. The resulting parameter values are then used in the model to predict concentrations at the messenger and POC wells for the next four quarters. Calibration and goodness-of-fit testing are discussed below.

A3.2.2 Goodness-of-fit Test (via Coefficient of Determination)

Two criteria must be met to verify that the data are sufficiently consistent with the first-order decay model:

1. The value of k obtained from the fitting process must be positive, indicating attenuation of the chemical over time.

2. The Coefficient of Determination of the regression (R^2) must be at least 0.80, indicating sufficiently good fit of the model to the data. In this context, R^2 is calculated as the square of the correlation coefficient between the measured concentration values and the corresponding values predicted by the model. Equation A3-6 is used to calculate R^2.

Equation A3-6.

$$R^2 = \left[\frac{\sum (C_i \hat{C}_i) - (\sum C_i)(\sum \hat{C}_i) / N}{(N-1) S_C S_{\hat{C}}} \right]^2$$

Where

Sums are all taken over i = 1,...N.

C_i	=	i^{th} measured concentration,
C^	=	Corresponding predicted value
S_C	=	Sample standard deviation of the N measured concentrations
$S_{\hat{C}}$	=	Sample standard deviation of the N corresponding predicted concentrations

The correlation coefficient (*r*) between two columns of numbers can easily be calculated directly by most popular spreadsheet software programs; the *r* value obtained must be squared to yield R^2.

If predictive data indicate a decreasing trend *and* R^2 $0.8, monitoring data should be collected over the next four quarters and compared with the model predictions. If either or both of these criteria are not met, the site is not appropriate for modeling. In such cases, closure may be pursued by (1) conducting stability monitoring (see Section A3.1), (2) collecting another four quarters of data and recalibrating the model (if the plume is stable), or (3) evaluating the plume using a nondefault approach.

Equation Set: (Ref: Introduction to Statistical Methods)

EQN 1 $C_p = C_0 \exp^{(-kt)}$

EQN 2 $$S = \sum_{t=0}^{N} \left[C_{pi} - C_0 \exp(-kt_i) \right]^2$$

EQN-3 $$R^2 = \left[\frac{\sum (C_m C_p) - (\sum C_m)(\sum C_p)/N}{(N-1) S_{C_m} S_{C_p}} \right]^2$$

ALSO,

EQN-3a $$R^2 = \left[\frac{S_{CmCp}}{\sqrt{S_{Cm} S_{Cp}}} \right]^2$$

EQN-3b $$S_C = \sum C^2 - \frac{\left(\sum C\right)^2}{N}$$

EQN-3c $$S_{CmCp} = \sum CmCp - \frac{\sum Cm \sum Cp}{N}$$

Where:

C_0	=	Initial Concentration (mg/l)
C_m	=	The measured concentration (mg/l)
C_p	=	The corresponding predicted concentration (mg/l)
S_{cm}	=	Sample standard deviation of the N measured concentrations
S_{Cp}	=	Sample standard deviation of the corresponding predicted concentrations
k	=	The attenuation rate (1/day)
t	=	Period of time between initial sample and sample C_m (days)
N	=	Number of measured samples

And,

S	=	First order minimization value
R^2	=	Coefficient of determination (correlation value)
RMSD	=	Root mean square deviation (prediction quality value)
S_c:		Defined by R^2, EQN-3a
S_{cmcp}:		Defined by R_2, EQN-3a

A3.2.3 Verification-Stage Monitoring by the Root-Mean-Square-Deviation Test

For verification modeling, samples are collected from the messenger wells for four more quarters. The Mann-Kendall trend test must be separately applied to the entire pool of data and to the last eight quarters of data for each COC at each well. If the trend continues to be stable or decreasing, verification modeling should be conducted.

Verification modeling by the Root-Mean-Square Deviation (RMSD) test measures how well the model predicts monitoring results after calibration. The RMSD is used for this comparison. Equation A3-7 is used to calculate the RMSD between a set of measured concentrations C_{mi} and the corresponding predicted concentrations C_{pi}.

Equation A3-7.

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n}(C_{mi} - C_{pi})^2}{N}}$$

The RMSD value is calculated using two sets of data:

1. The calibration data used to fit the model (Stage 1 data)

2. The monitoring-stage data (Stage 2 data), using the values of C and k obtained from Stage 1

The site will be eligible for closure only if the ratio of the Stage 2 RMSD to the Stage 1 RMSD is less than or equal to 1.3 ($RMSD_2/RMSD_1 \leq 1.3$).

In other words, the model fit can be no more than 30 percent worse during the monitoring stage than it was during the modeling stage.

If the dissolved contaminant plume meets these conditions, the site is eligible for closure. If not, then the following should be considered: (1) recalibrate the model using additional data, (2) pursue closure using stability monitoring, or (3) evaluate the plume using a nondefault approach.

An example of verification modeling by the RMSD test is provided below.

Assume that eight ground water samples have been collected with the following concentrations:

$$C_m = 90.1, 90.3, 73.4, 57.6, 64.7, 53, 54.2, 44.6$$

The first order minimization equation, Equation A3-5, requires that an iterative device (such as a computer program or a spreadsheet) be used to solve the equation. Using Table A3-3, solve for k using the RISC software.

Table A3-3. Initial Inputs for First 8 Quarters

Row/Col	A	B	C	D	E	F	G
1			Monitoring	Measured	First Order		
2	Co =	90.1	Time Period	Conc.	Prediction		
3	k =	0.0011	t	Cm	Cp	Cm - Cp	(Cm - Cp)^2
4			(Days)	mg/l	mg/l		
5			10	90.1	91.9	0	0
6			290	90.3	82.9	8.6	75
7			180	73.4	74.8	-0.6	0.3
8			270	57.6	67.6	-9.4	89
9			360	64.7	61	4	15.7
10			450	53	55	-2	4.2
11			540	54.2	49.7	4.3	18.7
12			630	44.6	44.8	-0.6	0.4
						Sum =	203.2

The RISC software will yield results similar to Table A3-4 below.

Table A3-4. Optimize Initial Inputs for First 8 Quarters

Row/Col	A	B	C	D	E	F	G	H
1			Monitoring	Measured	First Order			
2	**Co =**	91.86	Time Period	Conc.	Predictions			
3	**k =**	0.001	t	Cm	Cp	Cm - Cp	$(Cm - Cp)^2$	Cm*Cp
4			(Days)	mg/l	mg/l			
5			0	90.1	91.9	-1.76	3.1	8280
6			90	90.3	82.9	7.39	54.6	7486
7			180	73.4	74.8	-1.44	2.1	5490
8			270	57.6	67.6	-9.95	99	3894
9			360	64.7	61	3.73	13.9	3947
10			450	53	55	-2.04	4.2	2915
11			540	54.2	49.7	4.52	20.4	2694
12			630	44.6	44.8	-0.24	0.1	1998
		SUM =		527.9	527.7	0.21	197.4	36704

Cells B2 and B3 now contain the least-squares Co and k estimates.

Goodness of Fit Test

Beginning with the values in the above spreadsheet, we can now check the goodness of fit using the equations below. With the object of solving Equation A3-8a, we solve Equation-A3-8b and Equation A3-8c.

Example solving Equation A3-6b:

1. Sum C_m^2 = $90.1^2+90.3^2+73.4^2+57.6^2+64.7^2+53^2+54.2^2+44.6^2$ = 36,900
2. Sum C_m = 527.9
3. N = 8

$$Sc_m = 36900 - \left(\frac{527.9^2}{8}\right) = 2,065$$

In a similar manner, use Equation A3-8b to solve for Sc_p:

$Sc_p = 1898$

Example solving Equation A3-6c:

1. Sum C_mC_p = 36,704
1. Sum C_m = 527.9
1. Sum C_p = 527.7
1. N = 8

$$Sc_mc_p = 36704 - \left(\frac{527.9 * 527.7}{8}\right) = 1{,}882$$

Example using Equation A3-6a to solve for R^2:

$$R^2 = \left[\frac{1882}{\sqrt{1898 * 2065}}\right]^2 = 0.904$$

Because $R^2 = 0.9$ is greater than 0.8, the assessment can continue with an evaluation of the prediction results, using RMSDs.

Using Equation A3-4 and the optimized k and C_o values, predict the concentrations of the next four monitoring events, days 720 through 990.

$C_p = 40.5, 36.5, 33, 29.8$

Collect the next four monitoring samples and analyze. Assume that results are as follows:

$C_m = 49.5, 48.2, 40.9, 42.2$

Table A3-5 shows the new data.

Table A3-5. Prediction Inputs and Prediction Results

	Row/Col	A	B	C	D	E	F	G	H
INPUTS	1			Monitoring	Measured	First Order			
	2	**Co =**	91.86	Time Period	Conc.	Conc. Fit			
	3	**k =**	0.001	t	Cm	Cp	Cm - Cp	$(Cm - Cp)^2$	Cm*Cp
	4			(Days)	mg/l	mg/l			
	5			0	90.1	91.9	-1.76	3.1	8280
	6			90	90.3	82.9	7.39	54.6	7486
	7			180	73.4	74.8	-1.44	2.1	5490
	8			270	57.6	67.6	-9.95	99	3894
	9			360	64.7	61	3.73	13.9	3947
	10			450	53	55	-2.04	4.2	2915
	11			540	54.2	49.7	4.52	20.4	2694
	12			630	44.6	44.8	-0.24	0.1	1998
	13		**SUM =**		527.9	527.7	0.21	197.4	36704
RESULTS	14			720	49.5	40.5	9	81.5	
	15			810	48.2	36.5	11.7	136.1	
	16			900	40.9	33	7.9	62.8	
	17			990	42.2	29.8	12.4	154.6	
	18		**SUM =**					435	

Note: Beginning with row 14, the concentration predictions (C_p) are evaluated against the four monitoring events (C_m) conducted after the initial monitoring period using the mean square deviation $(C_m - C_p)^2$.

Calculate the RMSD for the model input period (the initial eight quarters), $RMSD_1$, using Equation A3-7:

$$RMSD1 = \sqrt{\frac{\sum_{i=1}^{n}(C_m - C_p)^2}{N}} = \sqrt{\frac{197.31}{8}} = 4.97$$

Calculate the RMSD for the model prediction results period (the final four quarters), $RMSD_2$, using Equation A3-7:

$$RMSD_2 = \sqrt{\frac{\sum_{i=1}^{n}(C_m - C_p)^2}{N}} = \sqrt{\frac{434.9}{4}} = 10.4$$

Evaluate the model predictions against the monitoring results using the

RMSDs: $RMSD_2$ / $RMSD_1$ = 2.1 > 1.3.

Because the attenuation model has not adequately predicted plume behavior, monitoring must continue, or another closure option should be pursued.